

# The Controlled Evolution of a Polymer Single Crystals

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## Introduction

Crystallization is an integral part of many processes and essential for the characterization of many materials, including small molecules, nanoclusters, and biological macromolecules [1,2]. For most crystallization processes, the ability to study the process is limited until the crystal reaches a critical size that allows one to observe it with spectroscopic or x-ray diffraction tools. Here we present a dip-pen nanolithography (DPN) method for controlling the initiation and kinetics of polymer crystal growth using atomic force microscope (AFM) tip coated with poly-DL-lysine hydrobromide (PLH). [3]

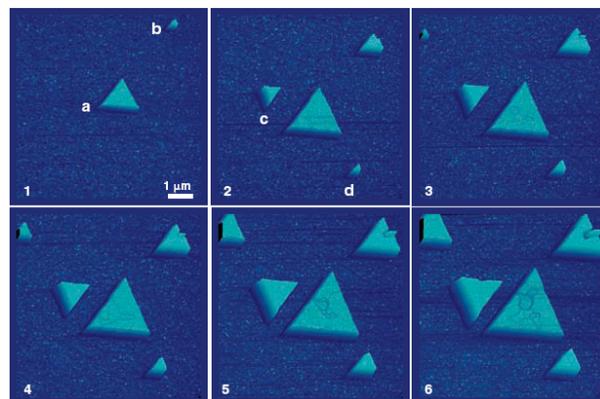
DPN allows an AFM tip to transport adsorbates to a surface in a controlled manner [4]. This technique has allowed researchers to control the nanoscale architecture of a surface and is compatible with both hard and soft materials. DPN coupled with AFM also can be used as a serial deposition tool to study monolayer formation. Polylysine, commonly used as a coating on inorganic substrates for the surface attachment of biomolecules and cells in molecular biology studies, is also regarded as a simple model for protein aggregation studies. We show how DPN initiates the crystallization of PLH on mica(001), 2M<sub>1</sub>-muscovite, and study and record the growth process from nanometer-sized seeds to larger crystalline structures as a function of environmental conditions.

## Methods and Materials

In a typical experiment, a PLH-coated silicon AFM tip is used as a deposition tool on a freshly cleaved mica (001) substrate in an AFM raster scanning experiment. The AFM was operated in tapping mode, during which the tip is oscillated at a frequency just below its resonant frequency (300 kHz). Tapping-mode AFM is more suitable than contact mode for imaging delicate polymer samples because it is less damaging to the sample.

## Results and Discussion

A single scan over an 8-by-8- $\mu\text{m}$  region of the mica surface results in the formation of two equilateral triangular prisms (a and b) that are substantially different in size (Fig. 1, panel 1). The smaller triangular feature (b) has a 320-nm edge length and is 21.8 nm thick, whereas the larger one (a) has a 1.62- $\mu\text{m}$  edge length and is 16.5 nm thick. The chemical composition of the triangular islands was confirmed by time-of-flight secondary ion mass spectroscopy, which exhibits the characteristic fragments for PLH. As the tip was scanned across the same area in tapping mode (scan rate, 2 Hz), one could observe the growth of seed crystals and the formation of new ones (compare panels 1 to 6 in Fig. 1). The growth process is very similar from crystal to crystal under these conditions. All observed structures were equilateral triangles, and crystals that were initiated at approximately the same time had nearly identical dimensions after the same number of raster scans.



**Fig. 1.** Panels 1 to 6 show a series of 8-by-8- $\mu\text{m}$  3D topographic AFM images taken at 256-s intervals (relative humidity, 30%; temperature, 20°C), obtained by continuously scanning an AFM tip coated with PLH molecules in tapping mode. Crystals (labeled as a, b, c, and d) were chosen for kinetic studies. PLH triangles with edge lengths ranging from 100 nm to 10  $\mu\text{m}$  and with heights from 5 to 50 nm were generated. From Ref. [3].

Growth of the PLH single crystals are an AFM tip induced effect and strongly depends on the delivery of the PLH molecules. The observed lateral and the height growth of the PLH prisms follows a simple scaling law. The growth scaling exponents show that the growth-rate along the lateral direction is much faster than the height growth. This can be attributed, in part, to the strong electrostatic PLH molecule-substrate interaction that accelerates the growth of the crystal along the lateral direction. Back reflection X-ray Laue patterns from the mica (001) combined with the optical microscopy revealed that the two opposing directions of the triangular prisms matched the underlying 2D pseudo-hexagonal symmetry of the mica (001) surface. This indicates orientational epitaxy. Single crystal oscillation XRD measurements in grazing-incidence geometry were carried out at the APS 5ID-C station. These measurements showed that the prisms were single crystal in nature.

This work represents a strategy for combining scanning-probe and x-ray methods to reveal the linkage between outer morphology and inner crystallography of nanoscale structures formed at the organic/inorganic interface.

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